RF-91-233 {6136}

**CORRELATIONS BETWEEN SURFACE STRUCTURE AND
CATALYTIC ACTIVITY/SELECTIVITY**

DOE/ER/13954--2

DE91 004230

PROGRESS REPORT

for Period October 1, 1989 - September 30, 1990

DE-FG05-88ER13954

D. W. Goodman

Department of Chemistry
Texas A&M University
College Station, TX 77843

NOVEMBER 1990

Prepared for
Department of Energy

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Report
MASTER
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

PROJECT DESCRIPTION

During the coming year we will continue to address those issues which are keys to understanding the relationship between surface structure and catalytic activity/selectivity. These issues also impact the understanding of the origins of the enhanced catalytic properties of mixed-metal catalysts. The experimental approach utilizes a microcatalytic reactor contiguous to a surface analysis system, an arrangement which allows in vacuo transfer of the catalyst from one chamber to the other. Surface techniques being used include Auger, UV and X-ray photoemission spectroscopy, temperature programmed desorption, low energy electron diffraction, high resolution electron energy loss spectroscopy and fourier transform infrared spectroscopy.

This research will build on this past year's work which has defined several metal overlayer systems regarding structural (LEED, XPS, IRAS), chemisorptive (TPD, HREELS), and catalytic (reaction kinetics) properties. We will concentrate further on the determination of the unique catalytic properties of these monolayer and submonolayer metal films. Of particular interest are those systems involving "active" catalytic metals, e.g. Ni, Ir, Pt, Co, Fe on "inactive" substrates, e.g. W, Re, Mo.

Work will continue on the investigation of methanol synthesis and the oxidation of carbon monoxide over copper and monolayer copper on rhodium. Recent data have shown a marked increase in the rate of the latter reaction (CO/O_2) on monolayer Cu films. Further work is planned to explore the unique properties of ultrathin copper films for the CO/NO reaction.

During the coming year we expect to finish the first phase of our efforts to simulate supported metal catalysts using metal deposits on thin oxide films. This work utilizes the deposition of a metal catalyst, e. g. Ni, Cu, onto a well-characterized thin oxide film of the support material, e. g. Al, Si, Mg. An array of electronic and chemical probes are being used to establish the validity of the support model while parallel electron microscopic studies are planned to characterize the nature of the metal deposits.

The IRAS work will continue with special emphasis on the morphology of mixed-metal systems. Work during the past year has shown that the use of probe molecules such as CO can provide unique information regarding the structure and specific site decoration that occurs upon the addition of one metal to a second. Of specific concern are the systems Ni/Mo and Co/Mo and the nature of these catalysts following sulfidation.

HREELS work will continue and be directed toward the study of the special chemical properties of monolayer metal films. Special attention will be given the energetics and bonding conformation of hydrocarbon intermediates related to the hydrogenolysis and rearrangement of organic precursors.

XPS, UPS, and ISS work currently in progress will proceed toward the understanding of the nature of the electronic modification found in metal overlayer systems compared to their bulk analogs and the relationship of these perturbations to the special chemistry exhibited by these systems.

CORRELATIONS BETWEEN SURFACE STRUCTURE AND
CATALYTIC ACTIVITY/SELECTIVITY

TABLE OF CONTENTS

	Page
I. SUMMARY OF PROGRESS	3
II. PUBLICATIONS CITING DOE/BES	6
III. RESEARCH ACCOMPLISHMENTS	10

Abstract removed

I. SUMMARY OF PROGRESS

Presently we have eight vacuum surface analytical/microreactors in operation manned by the PI, four postdoctoral associates, and eight graduate students. Six of these systems, three postdocs and five graduate students are dedicated to this DOE-BES project. Our range of capabilities include high resolution electron energy loss spectroscopy (HREELS), low energy electron diffraction (LEED), Auger spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), ion scattering spectroscopy (ISS), reflection absorption fourier transform infrared spectroscopy (IRAS), and temperature desorption spectroscopy (TDS). We also have an array of evaporators, ion guns, gas handling equipment, mass spectrometers, gas chromatographs, etc., for ancillary measurements and sample preparation. Each of the vacuum systems is interfaced to an individual PC for experiment control and data acquisition, and each is networked to a large central computer for data storage and manipulation. These facilities are housed in approximately 3000 square feet of newly renovated laboratory, office, and conference room space.

Several projects are underway which are examining the novel structure and chemistry of monolayer metal films, particularly regarding their use in delineating structural effects in catalysis. These are particularly exciting new materials whose electronic and chemical properties are essentially unexplored. In progress are studies on the electronic properties of these

materials using XPS and UPS. Recent work has shown a remarkable correlation between the measured surface core level shifts found for a number of overlayer systems and the corresponding perturbations found in the shift of the CO desorbing peak maximum from the bulk metal. Work is also taking place on the vibrational properties of CO, hydrogen, and hydrocarbons adsorbed onto thin metal overlayers using IRAS and HREELS.

Some very exciting studies are in progress using probe molecules such as CO to investigate the morphology of thin metal films using IRAS. Of particular interest at present is the nature of the sulfidation of Ni/Mo and Co/Mo catalysts and the relationship of the resulting structure to the special chemistry of these important bimetallic catalysts.

Kinetic studies are currently underway addressing the special catalytic properties of monolayer metal films. For example, recent work has shown that monolayer Cu on Rh catalyzes the CO/O₂ reaction at an order of magnitude faster rate than either Cu or Rh. This special activity can be related to the enhanced sticking coefficient of O₂ on the mixed metal catalyst under reaction conditions. These kinetic studies are presently being extended to address the unique properties of monolayer Cu films for the synthesis of methanol from hydrogen and CO.

The program during the past year has been extremely productive (see Section II), and the coming year promises to be even better. The program is staffed by excellent postdocs and students and is being carried out in laboratory facilities that

are absolutely first rate in all respects. The university is fully supportive of our program and is aggressively pursuing the goal of a world-class surface science center of excellence at Texas A&M University. This DOE-BES program will play a key role in this overall goal.

II. PUBLICATIONS ACKNOWLEDGING DOE-BES SUPPORT (ONLY FROM TEXAS
A&M UNIVERSITY), SEPT. 1989 - SEPT. 1990

106. "Nitrogen Adsorption on Re(0001) Studied by LEED, TPD, AES and ELS," J.-W. He and D. W. Goodman, Surface Sci. **218**, 211 (1989)
107. "Butane Hydrogenolysis on Rhodium Single Crystals," B. Hegarty, A. Datye, and D. W. Goodman, J. Chem. Soc., Faraday Discuss., **87**, 109 (1989).
108. "Copper Overlayers on Re(0001)," J.-W. He and D. W. Goodman, J. Phys. Chem., **94**, 1496 (1990).
109. "The Adsorption of Hydrogen, Carbon Monoxide and Nitrogen on Cu Overlayers on Re(0001)," J. -W. He and D. W. Goodman, J. Phys. Chem., **94**, 1502 (1990).
111. "The Role of Potassium Promoters in Nickel Catalysts for CO Hydrogenation," D. W. Goodman, Chapter in Physics and Chemistry of Alkali Metal Adsorption Edited by H. P. Bonzel, A. M. Bradshaw, and G. Ertl, Elsevier, 1989, p. 293.
112. "Surface Chemistry of Mixed-metal Systems," D. W. Goodman, in Metal-Metal Bonds and Clusters in Chemistry and Catalysis," Proc. IUCCP Conf., Texas A&M University, Ed. J. Fackler (Texas A&M Press, Austin, TX), 1989.
113. "Overlayer Growth and Chemisorptive Properties of Ultra-Thin Fe Films on W(110) and W(100)," J. -W. He, P. J. Berlowitz, and D. W. Goodman, Surface Sci., **231**, 315 (1990).
114. "Interaction of Borazine with a Re(0001) Surface, Studied by LEED, TDS, AES and ELS, J.-W. He and D. W. Goodman, Surface Sci., **232**, 138 (1990).
115. "The Role of Surface Structure in CO Hydrogenation on Cobalt," B. G. Johnson, C. H. Bartholomew, and D. W. Goodman, J. Catal., in press.
117. "Adsorption of CO and H₂ on Ultra-thin Films of Fe and Ni on Mo(110)," J.-W. He and D. W. Goodman, in preparation.
118. "The Effect of Sulfur on the Dissociative Adsorption of Methane on Nickel," Xudong Jiang and D. W. Goodman, Catal. Letts., **4**, 173 (1990).
119. "Surface Chemistry of Monolayer Metallic Films on Re(0001) and Mo(110)," J.-W. He, Wei-Lu Shea, Xudong Jiang, and D. W. Goodman, J. Vac. Sci. Technol., **8**, 2435 (1990).

120. "Dissociative Adsorption and Hydrogenolysis of Ethane over Clean and Ni Covered Pt(111)," Jose Rodriguez and D.W. Goodman, J. Phys. Chem., 94, 5342 (1990).
121. "Forazine Adsorption and Reaction on a Re(0001) Surface", J.-W. He and D.W. Goodman, Proceedings of the MRS Symposium on the Chemical Vapor Deposition of Refractory Metals and Ceramics, Eds. T. E. Besmann and B. M. Ballois, Pittsburgh, PA, vol. 168, p. 81, 1990.
122. "Dissociative Adsorption of Alkanes on Clean and Sulfur-Modified Nickel Surfaces," Xudong Jiang and D.W. Goodman, chapter in Applied Physics A, 51, 99 (1990).
123. "Surface Chemistry of Monolayer Metallic Films", D. W. Goodman, J. Ultramicroscopy, in press.
125. "Chapter III: Catalytic Activation of CO over Single Crystals," Jose Rodriguez and D. W. Goodman, in "New Trends in CO Activation," L. Guczi, ed.; (Elsevier, Amsterdam, 1990) Chapter III.
126. "The Oxidation of Carbon Monoxide on Rh(100) Under Steady State Conditions: An FT-IR Study," Lam-Wing Leung and D. W. Goodman, Catal. Letts., 5, 353 (1990).
127. "Adsorption of CO on Rh(100) Studied by Infrared Reflection-Absorption Spectroscopy (IRAS)," L.-W. Leung, J.-W. He and D. W. Goodman, J. Chem. Phys., in press.
128. "The Interaction of Ultrathin Films of Ni and Pd with W(110): An XPS Study," Robert Campbell, Jose Rodriguez, and D. W. Goodman, Surface Sci., in press.
129. "Electronic Interactions in Bimetallic Systems: An XPS Study," Jose Rodriguez, Robert Campbell, and D. W. Goodman, J. Phys. Chem., 94, 6936 (1990).
130. "The Adsorption and Decomposition of Methanol on the Rh(100) Surface," John Parmeter, Xudong Jiang, and D. W. Goodman, Surface Sci., in press.
131. "The Interaction of Ultrathin Films of Cu with Rh(100) and Ru(0001): An XPS Study," Jose Rodriguez, Robert Campbell, and D. W. Goodman, J. Phys. Chem., in press.
132. "IR Vibrational Studies of CO Adsorption on Ultra-thin Cu Films on a Rh(100) Surface," J.-W. He, Kevin Kuhn, L.-W. Leung, and D. W. Goodman, J. Chem. Phys., in press.
133. "Modeling the Metal-Solution Interface in Ultrahigh Vacuum: Vibrational Studies of the Coadsorption of Water and Carbon

Monoxide on Rh(100)," Lam-Wing H. Leung and D. Wayne Goodman, Langmuir, in press.

134. "The Adsorption and Decomposition of Methanol on Copper Overlayers on the Rh(100) Surface," Xudong Jiang, J. E. Parmeter, C. A. Estrada, and D. W. Goodman, Surface Sci., in press.

135. "Adsorption of CO, H₂, O₂, and CO₂ on Clean and Cu-covered Re(0001): An XPS Study," José A. Rodríguez, Robert A. Campbell and D. Wayne Goodman, Surface Sci., in press.

136. "An IR Study of CO Diffusion on Cu/Rh(100) J.-W. He, W. K. Kuhn and D. W. Goodman, J. Phys. Chem., submitted for publication.

138. "A IR Study of CO surface Diffusion on Submonolayer Metal Overlayers," W. K. Kuhn, J.-W. He, and D. W. Goodman, Chem. Phys. Letts., 172, 331 (1990).

139. "Ultra-thin Cobalt Films on Mo(110): Overlayer Growth and Chemisorption of CO and D₂," Jian-Wei He and D. W. Goodman, Surface Sci., in press.

140. "Surface Science Studies of the Electronic and Chemical Properties of Bimetallic Systems," Jose Rodriguez and D. W. Goodman, in preparation.

141. "Methanol Chemistry on Clean and Copper-covered Rh(100) Surfaces," J. E. Parmeter, X. Jiang, and D. W. Goodman, J. Vac. Sci. Technol., in press.

142. "Interaction of CO with Cu/Rh(100), Cu Overlayer Structures and CO Surface Diffusion," J.-W. He, W. K. Kuhn, L.-W. H. Leung, D. W. Goodman, J. Vac. Sci. Technol., in press.

143. "Correlations Between Structure and Reactivity of Metal Surfaces," Xudong Jiang and D. W. Goodman, Chapter in Studies in Surface Science and Catalysis, Eds. R. K. Grasselli and A. W. Sleight, Elsevier Publishers, 1990.

144. "Cu Titration of Tilted CO on a Mo(110) Surface," J.-W. He, W. K. Kuhn and D. W. Goodman, Chem. Phys. Letts., submitted for publication.

145. "Electronic Interactions in Bimetallic Systems: Core Level Binding Energy Shifts," J. A. Rodriguez, R. A. Campbell, and D. W. Goodman, J. Vac. Sci. Technol., in press.

146. "An AES, LEED, and CO Chemisorption Study of Copper Overlayers on the Rh(100) Surface," X. Jiang and D. W. Goodman, Surface Sci., submitted for publication.

147. "CO Oxidation on a Cu/Rh(100) Bimetallic Catalysts, J. Szanyi and D. W. Goodman, in preparation.

III. SELECTED RESEARCH ACCOMPLISHMENTS

A. CO Oxidation on a Cu/Rh(100) Bimetallic Catalysts

The oxidation of CO by O₂ on Cu(100), Rh(100), and a series of Cu/Rh(100) model bimetallic catalysts has been studied using a combined elevated pressure reactor - ultrahigh vacuum (UHV) surface analytical chamber. Experiments were carried out at 455K, at a total pressure of 10 Torr and with a stoichiometric CO/O₂ mixture. For these conditions the activity of the Cu(100) surface was found to be ~0.5 that of the Rh(100) surface. On the other hand, the activity of the Rh(100) surface was found to be markedly enhanced toward this reaction upon the addition of Cu. A maximum in catalytic activity was found for the Cu/Rh(100) bimetallic system at a Cu coverage of about ~1.3 monolayers (ML) (Fig. 1). A gradual decrease in catalytic activity was observed for Cu coverages in excess of 1.3 ML; however, the activity of the Cu/Rh(100) system was always higher than that of clean Rh(100) or Cu(100) even at Cu coverages >3 ML.

The surface composition as a function of reaction conditions was followed by Auger electron spectroscopy. An excellent correlation was found between the surface oxide present subsequent to reaction and the corresponding catalytic activity. At strongly oxidizing reaction conditions the thin Cu films cluster into 3-dimensional CuO islands, resulting in a sharp decrease in activity. The changes in surface composition and catalytic activity were found to be entirely reversible. That is, heating the surface to 750K (leading to the desorption of

oxygen) restored both the initial surface composition and catalytic activity.

*Publication No. 147 in DOE-BES Publication List (Section II)

Figure 1. Relative rate of reaction vs. surface Cu coverage on Rh(100) for CO oxidation.

B. The Electronic Properties of Bimetallic Surfaces Studied by X-ray Photoelectron Spectroscopy (XPS)

The electronic properties of Cu, Ni and Pd films supported on single-crystal metal surfaces have been examined by means of X-ray photoelectron spectroscopy (XPS). The shifts in core-level binding energies indicate that adatoms in a monolayer of Ni, Cu or Pd are electronically perturbed with respect to the surface atoms of Ni(100), Cu(100) or Pd(100). The present results show a correlation between the shifts in XPS surface core-level binding energies and variations in the desorption temperature of CO from metal adlayers (see Fig. 2). The shifts in XPS binding energies and CO desorption temperatures can be explained in terms of: (1) variations that occur in the admetal-admetal interactions when the admetal adopts the lattice parameters of the substrate; and (2) effects of the admetal-substrate interaction.

Chemisorption of CO induces a large decrease in the electron density of the metal adlayers. This is a consequence of: (1) charge transfer from the metal adlayer to the substrate (induced by a repulsive interaction between the admetal σ charge and electrons in the 5σ orbital of CO); and (2) transfer of electrons from the admetal into the 2π orbital of CO (π -back-bonding).

*Publications No. 128, 129, 131, 135, 140, 145 in DOE-BES

Publication List (Section II)

Figure 2. Correlation between the shift in surface core-level binding energy and the shift in CO TPD maximum. The properties of the Pd, Ni and Cu monolayers are compared with the corresponding values for the (100) face of the pure metals.

C. Reflection Absorption Spectroscopic (IRAS) Studies of Bimetallic Surfaces

The interaction of CO with ultra-thin metal films on single-crystal metal surfaces has been studied using infrared reflection adsorption spectroscopy (IRAS). The vibrational frequency of CO on Cu/Rh(100) at low Cu coverage (~0.1 ML) shows a blue shift relative to the CO gas phase stretching frequency (shown in Fig. 3). This blue shift is contrary to the red shift typically observed for CO adsorbed on metal surfaces. The shift likely arises from CO adsorbed onto Cu adatoms which are either slightly charged due to charge transfer from Cu to Rh, or self-polarized because of a strong Cu-Rh interaction.

Figure 3. IR spectra of CO on Cu/Rh(100). Cu was deposited at 100K, and the CO exposures and spectral collection were at 85K.

It is further shown that disordered Cu islands, well-ordered Cu pseudomorphic islands, and Cu 3-dimensional clusters are distinctively characterized by their CO peak frequencies. In addition, it is found that CO adsorbed onto ~0.1 ML Cu/Rh(100) will spill over from the Cu to the Rh at approximately 200K, and that Cu deposition onto a CO pre-covered Rh(100) surface at 95K causes CO spill-over from the Rh to the Cu, thus forming a CO/Cu/Rh(100) structure. Likewise, CO adsorbed on 0.14 ML Pd on W(100) will spill-over from the Pd to the W at approximately 200K (see Fig. 4).

Figure 4. IR spectra of CO on Cu/Rh(100) and Pd/W(110). The Cu and Pd overlayers were deposited at 100K, and the CO exposures were at a sample temperature ≤ 90 K. The IR spectra were collected at the indicated temperatures.

In a study of CO adsorption on Ni and Co films on a Mo(110) surface, it was seen that CO IRAS is a sensitive probe for studying transitions at the metal overlayer/substrate interface. LEED studies have shown that Ni/Mo(110) and Co/Mo(110) surfaces that have been annealed to ~ 900 K show phase transitions from the (8X2) to (7X2) and pseudomorphic to (9X2) structures at Ni and Co coverages of ~ 0.74 and ~ 1.0 ML, respectively. These phase transitions are clearly reflected in the CO IR spectra (see Fig. 5). In addition, the disorder-order transitions of Ni/Mo(110) and Co/Mo(110) are also indicated in the corresponding IR spectra. The transitions of the two dimensional ordered and

disordered phases appear to occur via an island growth mechanism with nucleation at the island edges.

When a clean Mo(110) surface is exposed to CO at 95K, the initial ~0.3 ML of CO does not exhibit a vibrational frequency in the 1800 - 2200 cm^{-1} , however, AES shows that there is a build up of C and O on the surface. This suggests that the CO is either decomposing, or is tilted with respect to the surface normal. Upon subsequent deposition of ~0.9 ML Cu at 95K followed by heating, IRAS shows that a portion of the invisible, tilted CO molecules diffuses onto the Cu overlayer and assumes a visible, upright bonding geometry. The remainder of the CO dissociates on the Mo(110) surface into atomic C and O.

*Publications No. 138, 142, 144 in DOE-BES Publication List
(Section II)

Figure 5. IR spectra of CO on Ni/Mo(110). Ni was deposited at 100K, flashed to 900K, and exposed to CO at 90K.

END

DATE FILMED

12 / 12 / 90